

Pilot-Plant Process for Starch Xanthide Encapsulated Pesticides

E. I. STOUT, B. S. SHASHA, and W. M. DOANE, *Northern Regional Research Center, Agricultural Research, Science and Education Administration, U.S. Department of Agriculture, Peoria, Illinois, 61604*

Synopsis

A small pilot-plant batch process for the encapsulation of pesticides with crosslinked starch xanthate (starch xanthide) has been developed. Multipound quantities of several encapsulated pesticides have been prepared that have slow-release properties. Products were made from starch xanthates of varying degrees of substitution (0.1 to 0.3) and with various crosslinking agents (H_2O_2 , $NaNO_2$, $NaOCl$, $NaClO_2$, and $FeCl_3$). Recovery of the pesticides as the encapsulated product ranged from 62% to nearly 100%. In a single experiment, processing water was recycled without apparent problems.

INTRODUCTION

The widespread use of pesticides has contributed greatly to the efficient production of crops. However, a number of environmental and performance problems have been encountered with the use of most pesticides. Recently, controlled-release pesticides have been proposed as a means to reduce the level of active agent required, for a more effective control of target organisms, to reduce toxicity on nontarget organisms, to reduce environmental pollution, and to extend the effective period of activity. A limited number of pesticides contained in either a polymer matrix or coating are being marketed as slow-release formulations. In a preliminary communication, Shasha et al.¹ reported the encapsulation of numerous pesticides in a starch xanthide (crosslinked starch xanthate) matrix. Efficiency of encapsulation of the pesticides was greater than 75% for most of the pesticides and was 90%–100% for many of them. One product, which contained the highly volatile S-propyl dithiocarbamate, showed extremely good shelf life as well as effective herbicidal activity. The nematicide 1,2-dibromo-3-chloropropane (DBCP) also had extended shelf life when encapsulated with starch xanthide; and when tested by Feldmesser and Shasha,² the nematicidal activity was extended considerably compared to technical DBCP. Doane et al.³ recently reported that the delayed incorporation of starch xanthide-encapsulated butylate was several times as active as butylate in the form of an emulsifiable concentrate (EC).

Another volatile thiocarbamate, S-ethyl dipropylthiocarbamate (EPTC), which is effective on many grasses and broadleaf weeds while being selective on many important crops, has been encapsulated with starch xanthide and evaluated in both greenhouse and field tests.⁴ The results showed that the encapsulated product not only reduced weed populations more than the emulsifiable concentrate but also controlled weed growth for a longer period. These promising preliminary results have shown the need for more extensive field studies and for

larger samples to be evaluated. This paper reports the pilot-plant preparation of multipound quantities of starch xanthide-encapsulated pesticides. Extensive evaluation of pesticidal efficacy in ongoing field tests will be reported in subsequent publications.

EXPERIMENTAL

Materials

Corn starch (10%–12% H₂O), sodium hydroxide (tech.), carbon disulfide (tech.), hydrogen peroxide (tech., 30%), acetic acid (tech.), sodium nitrite (tech.), sodium chlorite (reagent), butylate, EPTC, EPTC plus antidote, vernolate, molinate, pebulate, cycloate, and dimilin were used as received from the supplier.

Equipment

Sigma-Blade Mixer Reactor

A stainless steel, jacketed sigma mixer of 10-liter working capacity was used for xanthation and encapsulation reactions that yielded 1½ to 2½ lb of product. The reactor was cooled by passing cold water through the jacket during the reactions.

Ribbon Blender

A stainless steel, jacketed 1½-cu. ft ribbon blender (J. H. Day Co.) equipped with a double-ribbon agitator and a pneumatically controlled discharge gate was used for preparing products in quantities of 6.5 to 11 lb.

Dryer

A dryer was fabricated by mounting a cylindrical basket inside a 55-gal lever-lock drum on a 1-in. stainless steel (SS) shaft (Fig. 1). The basket was fabricated from 30 in. long by 1 in. angle iron (SS) and 16-in.-diameter ¼-in. disks (SS), which formed the frame, and this frame was covered with #316 (SS) screen

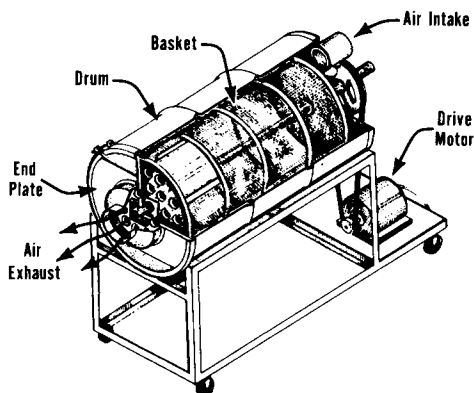


Fig. 1. Fabricated dryer.

(30 × 30 per linear in., 0.013-in.-diameter wire). The 16-in. disks were perforated with 25 1-in.-diameter holes, which were covered with the screen. The drum head was fitted with a 12 × 1/4 × 21 in.³ piece of sheet steel (SS) and nine holes of 1 1/2 in. diameter were spaced within a 5-in. radius from the center. A 4-in. opening was made in the opposite end of the drum to serve as an air intake. The unit was mounted horizontally on an iron frame and rotated at 50 rpm while a large volume of air was drawn through the unit by attaching an exhaust fan to the drum head. Samples of 20–30 lb of wet product were dried in 8–18 hr.

The center shaft on which the basket was mounted was extended 18 in. beyond the end of the drum, which allowed the drum to be opened and the basket to be extended beyond the end of the drum for filling and emptying.

Continuous Reactor

A continuous reactor, Baker–Perkins Flowmaster Rotofeed, was used for large-scale xanthations.

Attrition Mill

An 8-in. attrition mill, Bauer Bros. Co., Model 148-2 equipped with a #8319 plate was used to grind the wet encapsulated products (50%–75% H₂O) to give products of 14 to 30 mesh size. Some samples were more finely ground using plate No. 8114 such that all passed 20 mesh.

Procedures

Xanthations

The xanthation of starch was accomplished by one of two procedures—either a batch preparation in a ribbon blender or sigma-blade mixer, or a continuous process using a Baker–Perkins Flowmaster Rotofeed. A typical preparation of starch xanthate of D.S. 0.3 (D.S. is the average number of xanthate groups per repeating anhydroglucose unit) by the batch process is as follows. Starch (2950 g, 10% H₂O) was suspended in H₂O (18.16 kg) and CS₂ (640 ml) was added, followed by the addition of NaOH solution (640 g in 4.54 kg H₂O). The starch gelatinized immediately, and the resulting viscous mass was mixed slowly for 1 1/2 hr to allow the xanthation reaction to proceed.^{5,6}

Starch xanthate of D.S. 0.3 was prepared continuously by pumping a starch slurry (~14%), a sodium hydroxide solution (~14%), and carbon disulfide into the Flowmaster Rotofeed mixer in molar ratios of 1.0:1.0:0.76 starch:NaOH:CS₂, then storing the mixture at 25°C for 1 hr followed by storage at 5°C until needed. When molar ratios were 1.0:0.5:0.3, a xanthate of D.S. 0.19 resulted.

Encapsulation of Pesticides

Single Encapsulation

To a starch xanthate dispersion in the ribbon blender was added the pesticide, and the mixture was blended until a smooth dispersion was obtained (5 to 15 min). The pH of the mixture was then lowered by adding glacial acetic acid in

a molar amount equivalent to the total NaOH used in xanthation. After mixing for 3 to 5 min, 10 lb of ice was added followed by the addition of a solution of hydrogen peroxide (15%–30%) in an amount equivalent to $1\frac{1}{4}$ to $1\frac{1}{2}$ moles H_2O_2 per mole xanthate. The mixture, which turned to a rigid gel, was blended an additional 5 to 10 min, at which time it became a crumbly yellow solid of starch xanthide-encapsulated pesticide suspended in water. The mixture was removed from the reactor, filtered, and pressed to give a rubbery filter cake of 20% to 50% solids. This filter cake was then passed through the attrition mill with a setting such that 90%–100% of the product would pass through a 10-mesh screen which gave a product of the desired size when dry. The resulting product was then dried at room temperature (25–32°C) either by spreading the material on metal screens (SS) in a room of high air flow or in the dryer described previously. When the material was dried on stationary screens, it was necessary to hand mix the material every 15 to 60 min until the particles no longer stuck together on continued drying. After drying was complete (4 to 18 hr), that portion which was 14 to 30 mesh size was collected and a sample was tested in the laboratory for release of active agent. Pound quantities of the products were supplied to co-operating scientists for greenhouse and field studies.

For products prepared with crosslinking agents other than H_2O_2 , the amounts required were: 1 mole $FeCl_3$, 1 mole $NaNO_2$, 1 mole $NaClO_2$, or 2.5 mole $NaOCl$ per mole xanthate.

Double Encapsulation

Doubly encapsulated products were prepared by adding three fourths of the starch xanthate desired along with the total amount of pesticide and blending until a smooth dispersion was obtained. This mixture was then crosslinked as above. Then the remaining one-fourth of xanthate was added and the mixture was blended 3 to 5 min. Addition of acetic acid and hydrogen peroxide gave the yellow crumbly solid which was collected by filtration, ground, and dried in a manner similar to the procedure for single encapsulation.

Wet Test (Release Properties)

A 1.0-g sample of the encapsulated pesticide was placed on a watch glass in a fume hood, and 2.0-ml H_2O was added. The mixture was air dried 24 hr and weight loss was recorded. Every 24 hr, 2.0 ml more H_2O was added and the sample was redried. The wetting and drying procedure was usually repeated four times. The loss of pesticide was determined by analysis and corrected for weight loss.

The results were compared to a physical mixture of the pesticide and starch xanthide treated in a similar manner.

RESULTS AND DISCUSSION

A number of pesticides have been encapsulated in crosslinked starch xanthate matrix by a batch type process in 2- to 11-lb quantities. Total recovery of the pesticides from the reaction mixture as encapsulated products was 62% to 100%. Final products contained approximately 15% to 25% active pesticide and 75%

to 85% starch xanthide. All products reported in the tables were pulverized while wet to give the desired particle size.

The samples listed in Table I were prepared by crosslinking starch xanthate of D.S. 0.3 with hydrogen peroxide using the double encapsulation procedure. The recovery of the encapsulated pesticides was 80% to 95%. Additional pesticide could be recovered from the filtrate by allowing the filtrate to separate into two phases and decanting or by extracting the filtrate with an appropriate solvent such as hexane or carbon tetrachloride. The products all exhibited slower release of active agent than did commercial formulations as shown by the wet test. Earlier studies showed that results of wet tests correlated well with results from greenhouse evaluations. Previous preparations with comparable wet test results were effective for up to 90 days in control of target plants in greenhouse studies.⁴ Laboratory preparations of encapsulated pesticides that lost less than 20% of the pesticide in 96 hr had slow-release properties. The wet test results in Table I show a 5% to 20% loss for these products.

The pesticides were also singly encapsulated using starch xanthate of D.S. 0.3 with 76% to 83% recovery of pesticides, which is slightly lower than for the doubly encapsulated products (Table II). Wet test results indicated release properties to be equivalent to the doubly encapsulated products.

Starch xanthates of D.S. 0.2 were also used for encapsulation. Recovery shown in Table III ranged from 68% to nearly 100%. Wet test showed less loss of pesticide from these products over the 96-hr period than from the higher D.S. products, which suggests that these products should have slower release properties.

A sample of encapsulated EPTC was separated into four fractions of different particle size (Table IV). Nitrogen analysis showed that the larger particles

TABLE I

Double Encapsulation of Pesticide Emulsifiable Concentrates Using Starch Xanthate of D.S. 0.3

Pesticide	% Active in product	% Active recovered	Wet test % loss, 96 hr
Butylate	17.0	81	16
Butylate	18.9	86	5
Butylate-plus	14.9	95	—
Butylate	18.0	85	—
Butylate	18.8	81	5
EPTC	21.3	88	—
EPTC	21.3	88	19
Vernolate	18.0	82	—
Vernolate	21.5	80	20

TABLE II

Single Encapsulation of Pesticide Emulsifiable Concentrates Using Starch Xanthate of D.S. 0.3

Pesticide	% Active in product	% Active recovered	Wet test % loss, 96 hr
EPTC	22.0	77	20
EPTC	24	85	15
Vernolate	22	76	1
Butylate (tech.)	23	81	7
EPTC	23.8	83	14

TABLE III
Single Encapsulation of Pesticide Emulsifiable Concentrates Using Starch Xanthate of D.S. 0.2

Pesticide	% Active in product	% Active recovered	Wet test % loss, 96 hr
Cycloate	22.0	84	0
Cycloate	24.0	83	—
Butylate	21.4	90	3
Butylate-plus	20.0	73	6
Butylate-plus	19.5	85	5
EPTC	24.0	89	12
Vernolate	22.5	96	4
Surpass	20.0	74	9
Pebulate	18.0	90	3
Pebulate	18.0	68	—
Dimilin	10	100 ^a	—
EPTC-plus	16	81	13

^a Recovery estimated.

TABLE IV
Effect of Particle Size on EPTC-Plus Retention

Particle size	% N	% EPTC-plus
>14 Mesh	1.75	23.6
14-26 Mesh	1.76	23.8
<26 Mesh	1.63	22.0
<60 Mesh	1.39	18.8

contained higher concentration of pesticide. Analysis of other preparations gave similar results. Thus, as the xanthide precipitate is pulverized, some of the capsules are ruptured; this allows the volatile pesticides to be exposed and to evaporate. The loss is much greater if the dry product is pulverized. These results indicate that when the capsules are ruptured while wet, some of them may re-form on drying and therefore retain more of the pesticide. But when the capsules are ruptured in the dry state, the capsules cannot re-form, and some of the pesticide evaporates.

Table V shows the loss of pesticide from a physical mixture of starch xanthide and each of four pesticides added at a 20% level based on weight of starch xanthide and treated with water as in the wet test procedure. As expected, the rate of pesticide loss correlates with the vapor pressure, and the loss of pesticide is much higher than for the encapsulated products.

The products in Tables I through IV were prepared by crosslinking the xanthate with hydrogen peroxide. In addition, products have been prepared using

TABLE V
Loss of Pesticide from Physical Mixtures with Starch Xanthide

Pesticide	Vapor pressure, mm at 25°C	% Pesticide lost	
		24 hr	72 hr
EPTC	34×10^{-3}	85	94
Cycloate	6.2×10^{-3}	15	32
Vernolate	10.4×10^{-3}	40	89
Butylate	13×10^{-3}	75	96

TABLE VI
Encapsulation of Pesticide Emulsifiable Concentrates with Starch Xanthate and Various Crosslinking Agents

Pesticide	Xanthate D.S.	Oxidant	% Active in product	% Active recovered
EPTC-plus	0.20	NaOCl	15	62
Vernolate	0.13	FeCl ₃	27	90
EPTC	0.12	NaNO ₂	22	66
EPTC	0.12	NaClO ₂	25	74
2,4-D Ester	0.3	H ₂ O ₂	10	98
Picloram	0.3	H ₂ O ₂	9	98
2,4-D Ester	0.12	FeCl ₃	9	—

other oxidants for the crosslinking reaction (Table VI). Xanthates of D.S. 0.3, when crosslinked with H₂O₂, gave firm hard granules after grinding in the Bauer mill that were easily dried if the temperature of the mixture was kept below 32° during the crosslinking reaction. Xanthate of D.S. 0.2 gave softer particles, which contained more water and tended to stick together as the samples dried. Therefore, the samples were more difficult to handle and slower to dry. Xanthates of D.S. less than 0.15 retained too much water to be usable when H₂O₂ was the oxidant. However, if either NaClO₂, FeCl₃, or NaNO₂ was used for crosslinking xanthates of D.S. 0.10 to 0.15, products with physical properties similar to the D.S. 0.3, H₂O₂-crosslinked product were obtained.

A preparation of EPTC-plus was made in which the filtrate from the previous run was used for the makeup water in the xanthation step. No difficulties were encountered. Xanthation proceeded normally, although the color was a much brighter yellow, and the encapsulated products retained 76% of the pesticide. These results would indicate that the wastewaters may be recycled with no apparent problems. Another 15% of the pesticide was extracted from the filtrate, making total recovery 91%.

In conclusion, a small pilot-plant batch process for the encapsulation of pesticides with starch xanthide has been developed. Multipound quantities of encapsulated products are prepared in a single batch. Products were made from starch xanthates of varying degrees of substitution (0.1 to 0.3) and with various crosslinking agents (H₂O₂, NaNO₂, NaClO₂, NaOCl, and FeCl₃).

The authors wish to thank L. D. Miller and W. L. Williams for preparation of starch xanthate dispersions. This paper reports the results of research only. Mention of a pesticide does not constitute a recommendation for use by the U.S. Department of Agriculture nor does it imply registration under FIFRA as amended. Also, mention of firm names does not constitute an endorsement by the U.S. Department of Agriculture over other firms not mentioned.

References

1. B. S. Shasha, W. M. Doane, and C. R. Russell, *Polym. Lett.*, **14**, 417 (1976).
2. J. Feldmesser and B. S. Shasha, in *Proceedings of 1977 Controlled Release Pesticide Symposium*, Corvallis, Oregon, August 22-24, 1977.
3. W. M. Doane, B. S. Shasha, and C. R. Russell, *ACS Symp. Ser.* **53**, 74-83 (1977).
4. M. M. Schreiber, in *Proceedings of Meeting North Central Weed Control Conference*, Omaha, Nebraska, December 7-9, 1976.
5. D. Trimmell, W. M. Doane, C. R. Russell, and C. E. Rist, *Staerke*, **18**, 36 (1966).
6. E. B. Lancaster, L. T. Black, H. F. Conway, and E. L. Griffin, Jr., *Ind. Eng. Chem., Prod. Res. Dev.*, **5**, 354 (1966).

Received April 6, 1978